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(54) Title: IMPROVED POST PLASMA ASHING WAFER CLEANING FORMULATION			
(57) Abstract A semiconductor wafer cleaning formulation for use in post plasma ashing semiconductor fabrication comprising the following components in the percentage by weight ranges shown: chelating agen 2-98 %; solvent 2-98 %. In the preferred embodiment the chelating agent is selected from the group consisting of 2,4-Pentanedione, Malonic acid, Oxalic acid, p-Toluenesulfonic acid, and Trifluoroacetic acid and the solvent is selected from the group consisting of <u>Water</u> , Ethylene glycol, N-Methylpyrrolidone (NMP), Gamma butyrolactone (BLO), and Butyl carbitol.			

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Specification

IMPROVED POST PLASMA ASHING WAFER CLEANING FORMULATION

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation in part application which claims priority of U.S. Patent Application Serial No. 08/675,500, filed July 3, 1996, entitled: Post Plasma Ashing Wafer Cleaning Formulation, naming Thomas J. Kloffenstein and Daniel N. Fine as inventors.

BACKGROUND OF THE INVENTIONField of the Invention

10 The present invention relates generally to chemical formulations used in semiconductor wafer fabrication and particularly to chemical formulations that are utilized to remove residue from wafers following a resist plasma ashing step.

Description of the Prior Art

15 The prior art teaches the utilization of various chemical formulations to remove residue and clean wafers following a resist ashing step. Generally, these prior art chemical formulations include strong reagents such as strong acids, strong bases and/or highly reactive amine containing compounds. Such strong reagents can cause
20 unwanted further removal of metal or insulator layers remaining on the wafer and are therefore undesirable in many instances. A particular problem with strippers containing both amine component(s) and water is corrosion of metal, particularly aluminum and aluminum-copper alloys. There is therefore a need for chemical formulations which effectively remove residue following a resist ashing step which do not attack and potentially degrade delicate structures which are meant to remain on a wafer.

SUMMARY OF THE INVENTION

25 A semiconductor wafer cleaning formulation for use in post plasma ashing semiconductor fabrication comprising the following components in the percentage by weight ranges shown:

chelating agent

2 - 98%

solvent

2 - 98%

→ In the preferred embodiment the chelating agent is selected from the group consisting of 2,4-Pentanedione, Malonic acid, Oxalic acid, p-Toluenesulfonic acid, and Trifluoroacetic acid and the solvent is selected from the group consisting of Water, Ethylene glycol, N-Methylpyrrolidone (NMP), Gamma butyrolactone (BLO), and Butyl carbitol.

It is an advantage of the present invention that it effectively removes inorganic residues following a plasma ashing step.

It is another advantage of the present invention that it effectively removes metal halide and metal oxide residues following plasma ashing.

It is a further advantage of the present invention that it effectively removes inorganic residue from a semiconductor wafer following plasma ashing without containing a strong acid, strong base and/or amine containing compound.

These and other features and advantages of the present invention will become understood to those of ordinary skill in the art upon review of the following detailed description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical steps in the fabrication of semiconductor wafers involve the creation of a metalized layer having a patterned resist layer formed thereon. Such a wafer may then be exposed to a metal etching plasma (such as a halogen based plasma) to remove exposed metal. Thereafter, a plasma ashing step often is conducted (typically using an oxygen based plasma) in which the remaining resist is removed from the wafer. The result is a patterned metalized layer.

This series of steps generally results in a residue which must be removed from the wafer prior to further fabrication steps. The residue following the plasma ashing step is predominantly composed of inorganic compounds such as metal halides and metal oxides.

Various chemical formulations are currently used to remove the inorganic compound residues. These formulations are generally holdovers from older semiconductor fabrication wet chemical resist removal processes that were used prior to the introduction of the resist plasma ashing technology. The prior formulations thus typically contain strong acids or strong bases or highly reactive amine compounds to remove residues that remained following the wet chemical resist removal step.

The present invention comprises chemical formulations for the removal of inorganic compound residues, where the formulations do not contain strong acids, strong bases and/or reactive amine compounds of the prior art formulations. The general formulation of the present invention has two or three components that are present in the following ranges (where the percent (%) given is percent by weight):

5	Organic Chelating Agent	1 - 15%
	Water	25 - 99%
	Polar Organic Solvent	0 - 60%

A preferred general formulation is created where the organic chelating agent is Catechol (1, 2-dihydroxybenzene) and the polar organic solvent is Gamma butyrolactone (BLO). Thus, a preferred general formulation is:

10	Catechol	1 - 15%
	Water	25 - 99%
	BLO	0 - 60%

As is seen from the above formulation ranges, a first included series of formulations exists where there is zero BLO (BLO 0%). That is, a formulation of Catechol 1-10% and water 90-99%. Within these parameters a

15 preferred formulation comprises:

	Catechol	7 - 10%
	Water	90 - 93%

Regarding the three component formulations described above, a preferred three component formulation within the range of parameters is:

20	Catechol	7 - 12%
	Water	48 - 83%
	BLO	10 - 40%

Both preferred formulations have been shown to be effective in removing inorganic compound residues following plasma ashing of the resist. The following examples describe the utilization of the preferred

25 formulations.

Example I

A first example of the present invention involved wafers having 3-layer metal lines containing a top layer of titanium nitride (1200Å thick), a middle layer of aluminum (99.5%) copper (0.5%) alloy (10,000Å thick), and a

bottom layer of Titanium/Tungsten alloy (1500Å thick). The substrate was silicon oxide and the width of metal lines was approximately 0.8 microns.

The wafers were metal-etched with a chlorine-containing plasma which was followed by an oxygen plasma ashing of the resist. This was followed by immersion of the wafers in a bath of the present invention containing catechol 10%, water 50% and BLO 40% at 60°C for 30 minutes followed by washing with deionized water. Further testing has demonstrated that effective residue removal is obtained in a temperature range of 45° to 75°C, and with wafer exposure times in a range of 15 to 60 minutes. Additionally, rather than utilizing wafer immersion techniques, the solutions could be sprayed onto the wafers using automated spray tools followed by a water rinse.

Example II

A second set of wafers which were identical to the set utilized in Example I, were processed utilizing a different cleaning formulation. Specifically, the wafers were metal-etched with a chlorine-containing plasma which was followed by an oxygen plasma ashing of the resist. This was followed by immersion of the wafers in a bath of the present invention containing catechol 8% and water 92%, at 60°C for 30 minutes followed by washing with deionized water. As with the prior example, a formulation temperature of 45 to 75°C with a wafer exposure time of 15 to 60 minutes will produce satisfactory results.

Regarding both examples above, inspection of SEM photomicrographs of processed wafers was utilized to evaluate the stripping effectiveness of the formulations and also to confirm lack of corrosivity to metal features.

To someone of ordinary skill in the art it would be expected that chelating agents related to catechol and other polar organic solvents may also be utilized with comparable results. Catechol-related chelating agents would include derivatives of benzene, naphthalene, and aromatic heterocyclic compounds having at least two hydroxyl (OH) groups on adjacent carbon atoms. Other polar organic solvents which could be utilized include N-Methylpyrrolidone (NMP); Sulfolane; Propylene glycol monomethylether acetate (PMA); Ethylene glycol and propylene glycol; and Dimethylsulfoxide.

Additional formulations have been developed for stripping wafer residues which originate from plasma metal etching followed by ashing. The additional formulations utilize the following components (percentages are by weight):

A chelating agent compound	2-98%
Water and/or a polar organic solvent	2-98%

The preferred chelating agent compounds are:

2,4-Pentanedione	0-98%
Malonic acid	0-10%
Oxalic acid	0-5%
p-Toluenesulfonic acid	0-10%
Trifluoroacetic acid	0-12%

Other chelating agents that provide good results are:

Acetoacetamide	0-15%
Anthranilic acid	0-13%
Methyl acetoacetate	0-10%
Dimethylmalonate	0-10%
Boric acid	0-5%
Lactic acid	0-5%
Levulinic acid	0-5%

The preferred polar organic solvents are:

Water	0-98%
Ethylene glycol	0-98%
N-Methylpyrrolidone (NMP)	0-98%
Gamma butyrolactone (BLO)	0-40%
Butyl carbitol	0-59%

Preferred solvent formulations that are utilized in the specific cleaning formulations set forth below are:

Mixtures of NMP (50-55%) and water (28-40%)

Mixtures of BLO (40-50%) and water (30-50%)

A significant feature of the new formulations is the use of a chelating agent in a solvent solution which does not contain any amine or strong base.

Specific cleaning formulations include:

2,4-Pentanedione	10%
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	BLO	40%
	Water	50%
	2,4-Pentanedione	10%
5	NMP	50%
	Water	40%
	Oxalic acid	5%
10	NMP	55%
	Water	40%
	Methyl acetoacetate	10%
	BLO	40%
15	Water	50%
	Malonic acid	5-10%
	NMP	50-55%
	Water	40%
20	Malonic acid	5%
	BLO	50%
	Water	45%
25	p-Toluenesulfonic acid	10%
	NMP	50%
	Water	40%
	Trifluoroacetic acid	10%

NMP

50%

Water

40%

Other 1,3-dicarbonyl compounds and related compounds are expected to display comparable performance. These would have the following general structure:

→ -CHR-Y in which

R is either a hydrogen atom or an alkyl group and

X and Y are functional groups containing multiply bonded moieties known to have electron-withdrawing properties, for example X and Y may be CZ=O, C=N, CZ=N, CZ=S, NZ=O, SZ=O in which Z represents another atom or group of atoms. X and Y may be identical or different.

Other non-amine polar organic solvents are expected to be suitable either along or when mixed with water.

It would also be expected that inclusion of optional components such as surfactants, stabilizers, corrosion inhibitors, buffering agents, and cosolvents would constitute obvious additions to those practiced in the art.

Commercially generated wafers which have been etched with chlorine- or fluorine-containing plasmas followed by oxygen plasma ashing have residues that typically contain inorganic materials such as, but not limited to, aluminum oxide and titanium oxide. These residues are often difficult to dissolve completely without causing corrosion of metal and titanium nitride features required for effective device performance.

Four types of commercially generated wafers containing vias and metal lines were processed using the formulation of the present invention. In each case, following plasma etching and ashing, the residue was removed from the wafer by immersion of wafers in baths at 60° C for 30 minutes followed by washing with deionized water and drying with a stream of nitrogen gas. It is expected that the solutions can also be applied by spraying onto the wafers in an automated spray tool followed by a water rinse.

The four via and metal line structures were:

1. 0.8 micron diameter, four layer vias comprised of silicon oxide top and second layers, a third layer of titanium nitride, and a bottom layer of aluminum, silicon, copper (AlSiCu) alloy. The substrate was silicon oxide.
2. One micron diameter, two-layer vias comprised of a top layer of silicon oxide (7000 Angs. thick) and a middle layer of titanium nitride (1200 Angs. thick) on top of a silicon substrate.

3. 1.2 micron wide, 4-layer metal lines with a top layer of titanium/tungsten (1200 Angs. thick), a second layer of aluminum (6000 Angs. thick), a third layer of titanium/tungsten (1200 Angs thick), and a bottom layer of titanium (500 Angs. thick) on a silicon oxide substrate.

5 4. Two micron wide, 3-layer metal lines with a top layer of titanium (200 Angs. thick), a middle layer of aluminum/silicon/copper (750 Angs. thick), and a bottom layer of titanium/tungsten (1250 Angs. thick) on a silicon oxide substrate.

Based on inspection of scanning electron microscope photographs of customer wafers before and after treatment, the preferred formulations successfully removed residues without signs of corrosion on metal and/or alloy layers.

10 While the present invention has been shown and described with reference to particular preferred embodiments, it is to be understood that other and further changes and modifications of the invention will become apparent to those skilled in the art after understanding the present invention. It is therefore intended that the following claims cover all such alterations and modifications as fall within the true spirit and scope of the invention.

15

What I claim is:

CLAIMS

1. A semiconductor wafer cleaning formulation for use in post plasma ashing semiconductor fabrication comprising the following components in the percentage by weight ranges shown:

chelating agent	2 - 98%
solvent	2 - 98%
2. A cleaning formulation as described in claim 1 wherein said chelating agent is selected from the group consisting of, 2,4-Pentanedione, Malonic acid, Oxalic acid, p-Toluenesulfonic acid, and Trifluoroacetic acid.
3. A cleaning formulation as described in claim 1 wherein said chelating agent is selected from the group consisting of, Acetoacetamide, Anthranilic acid, Methyl acetoacetate, Dimethylmalonate, Boric acid, Lactic acid, and Levulinic acid.
4. A cleaning formulation as described in claim 1 wherein said chelating agent in the percentage by weight range shown is selected from the group consisting of, 2,4-Pentanedione 0-98%, Malonic acid 0-10%, Oxalic acid 0-5%, p-Toluenesulfonic acid 0-10%, and Trifluoroacetic acid 0-12%.
5. A cleaning formulation as described in claim 1 wherein said solvent is selected from the group consisting of, Water, Ethylene glycol, N-Methylpyrrolidone (NMP), Gamma butyrolactone (BLO), and Butyl carbitol.
6. A cleaning formulation as described in claim 1 wherein said solvent in the percentage by weight range shown is selected from the group consisting of, Water 0-98%, Ethylene glycol 0-98%, N-Methylpyrrolidone (NMP) 0-98%, Gamma butyrolactone (BLO) 0-40%, and Butyl carbitol 0-59%.
7. A semiconductor wafer cleaning formulation for use in post plasma ashing semiconductor fabrication, wherein said formulation in the percentage by weight ranges shown is selected from the group consisting of:

	2,4-Pentanedione	10%
	BLO	40%
	Water	50%,
5	2,4-Pentanedione	10%
	NMP	50%
	Water	40%,
10	Oxalic acid	5%
	NMP	55%
	Water	40%,
15	Methyl acetoacetate	10%
	BLO	40%
	Water	50%,
	Malonic acid	5-10%
	NMP	50-55%
20	Water	40%,
	Malonic acid	5%
	BLO	50%
	Water	45%,
25	p-Toluenesulfonic acid	10%
	NMP	50%

Water

40%, and

Trifluoroacetic acid

10%

NMP

50%

5

Water

40%

8. A method for fabricating a semiconductor wafer which includes the steps comprising:
plasma ashing a substance from the surface of the wafer;
cleaning said wafer in a following step using a chemical formulation comprising the following components in the percentage by weight ranges shown:
- 5 chelating agent 2 - 98%
solvent 2-98%
9. A method as described in claim 8 wherein said chelating agent is selected from the group consisting of: 2,4-Pentanedione, Malonic acid, Oxalic acid, p-Toluenesulfonic acid, Trifluoroacetic acid.
10. A method as described in claim 8 wherein said chelating agent is selected from the group consisting of: Acetoacetamide, Anthranilic acid, Methyl acetoacetate, Dimethylmalonate, Boric acid, Lactic acid, and Levulinic acid.
11. A method as described in claim 8 wherein said chelating agent in the percentage by weight range shown is selected from the group consisting of, 2,4-Pentanedione 0-98%, Malonic acid 0-10%, Oxalic acid 0-5%, p-Toluenesulfonic acid 0-10%, and Trifluoroacetic acid 0-12%
12. A method as described in claim 8 wherein said solvent is selected from the group consisting of: Water, Ethylene glycol, N-Methylpyrrolidone (NMP), Gamma butyrolactone (BLO), and Butyl carbitol.

13. A method as described in claim 8 wherein said solvent in the percentage by weight range shown is selected from the group consisting of, Water 0-98%, Ethylene glycol 0-98%, N-Methylpyrrolidone (NMP) 0-98%, Gamma butyrolactone (BLO) 0-40%, and Butyl carbitol 0-59%.

14. A method as described in claim 9 wherein said cleaning formulation in the percentage by weight ranges shown is selected from the group consisting of:

2,4-Pentanedione	10%
BLO	40%
Water	50%,

2,4-Pentanedione	10%
NMP	50%
Water	40%,

Oxalic acid	5%
NMP	55%
Water	40%,

Methyl acetoacetate	10%
BLO	40%
Water	50%,

Malonic acid	5-10%
NMP	50-55%
Water	40%,

	Malonic acid	5%
	BLO	50%
	Water	45%,
5	p-Toluenesulfonic acid	10%
	NMP	50%
	Water	40%, and
	Trifluoroacetic acid	10%
10	NMP	50%
	Water	40%.

15. A method for fabricating a semiconductor wafer including the steps comprising:

plasma etching a metalized layer from a surface of the wafer;

plasma ashing a resist from the surface of the wafer following the metal etching step;

cleaning the wafer in a following step using a chemical formulation including the following components in the

5 percentage by weight ranges shown:

chelating agent 2 - 98%

solvent 2 - 98%.

16. A method as described in claim 15 wherein said chelating agent is selected from the group consisting of: 2,4-Pentanedione, Malonic acid, Oxalic acid, p-Toluenesulfonic acid, Trifluoroacetic acid.

17. A method as described in claim 15 wherein said chelating agent is selected from the group consisting of: cetoacetamide, Anthranilic acid, Methyl acetoacetate, Dimethylmalonate, Boric acid, Lactic acid, and Levulinic acid.

18. A method as described in claim 15 wherein said chelating agent in the percentage by weight range shown is selected from the group consisting of, 2,4-Pentanedione 0-98%, Malonic acid 0-10%, Oxalic acid 0-5%, p-Toluenesulfonic acid 0-10%, and Trifluoroacetic acid 0-12%

19. A method as described in claim 15 wherein said solvent is selected from the group consisting of: Water, Ethylene glycol, N-Methylpyrrolidone (NMP), Gamma butyrolactone (BLO), and Butyl carbitol.

20. A method as described in claim 15 wherein said solvent in the percentage by weight range shown is selected from the group consisting of, Water 0-98%, Ethylene glycol 0-98%, N-Methylpyrrolidone (NMP) 0-98%, Gamma butyrolactone (BLO) 0-40%, and Butyl carbitol 0-59%.

21. A method as described in claim 15 wherein said cleaning formulation in the percentage by weight ranges shown is selected from the group consisting of:

2,4-Pentanedione	10%
BLO	40%
Water	50%,

2,4-Pentanedione	10%
NMP	50%
Water	40%,

Oxalic acid	5%
NMP	55%
Water	40%,

Methyl acetoacetate	10%
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	BLO	40%
	Water	50%,
	Malonic acid	5-10%
5	NMP	50-55%
	Water	40%,
	Malonic acid	5%
	BLO	50%
10	Water	45%,
	p-Toluenesulfonic acid	10%
	NMP	50%
	Water	40%, and
15	Trifluoroacetic acid	10%
	NMP	50%
	Water	40%.

22. A method as described in claim 8 wherein the wafer is exposed to said chemical formulation for a time period of 15-60 minutes at a temperature range of 45-75°C.

23. A method as described in claim 15 wherein the wafer is exposed to said chemical formulation for a time period of 15-60 minutes at a temperature range of 45-75°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12421

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B08B 3/04, 3/08, 3/10, 7/00, 7/04; C11D 7/22, 7/50, 7/60

US CL : 134/1.2, 1.3, 2, 3, 38, 40, 42; 510/175, 176, 178

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 134/1.2, 1.3, 2, 3, 38, 40, 42; 510/175, 176, 178

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,183,552 A (BRESSEL et al) 02 February 1993, entire document, especially column 5, lines 43-52.	1, 2 and 4-6 ----- 3 and 7
X --- Y	US 5,334,332 A (LEE) 02 August 1994, entire document.	1, 5, 6, 8, 12, 13, 15, 19, 20, 22 and 23 ----- 2-4, 7, 9-11, 14, 16-18 and 21
X --- Y	US 5,466,389 A (ILARDI et al) 14 November 1995, entire document.	1 and 5 ----- 2-4 and 6-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

29 AUGUST 1997

Date of mailing of the international search report

24 SEP 1997

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12421

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,744,834 A (HAQ) 17 May 1988, entire document.	1-23
X — Y	US 5,236,552 A (FANG) 17 August 1993, entire document, especially column 3, lines 10-39.	1, 2 and 4-6 3 and 7-23
X — Y	US 4,221,674 A (VANDER MEY) 09 September 1980, entire document.	1, 2 and 4 3 and 7-23

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12421

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS search terms: pentanedione, malonic, oxalic, toluenesulfonic, trifluoroacetic, acetoacetamide, anthranilic, borio, lactic, levulinic, dimethylmalonate, acid, water, aqueous, nmp, methylpyrrolidone, butyrolactone, bio, butyl carbitol, ethylene glycol, wafer, plasma, semiconductor, resist, photoresist.